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Carbonate deposition and benthic $\delta^{13}C$ in the subarctic Pacific: implications for changes of the oceanic carbonate system during the past 750,000 years

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ABSTRACT

Carbonate deposition at two core sites in the subarctic Pacific (48° N, 133° W; 2.9 km and 3.7 km water depth) follows the standard Pacific carbonate cycles, with glacial values being increased over interglacial values. Benthic $\delta^{13}C$ follows the global trend; that is, glacial values are more negative than interglacial values. Comparison with the benthic $\delta^{13}C$ record of North Atlantic DSDP Site 552 (56° N, 23° W; 2.3 km water depth) shows the North Pacific records to be nearly in phase with and continuously more negative relative to the North Atlantic record. This suggests that concentrations of $\Sigma CO_{2(org)}$ were permanently higher in the North Pacific than in the North Atlantic during the past 750,000 years conceivably supporting the hypothesis that there was no deep-water forming in the late Pleistocene North Pacific. Whereas one would expect that the North Pacific deep waters were continuously more corrosive to carbonates than deep waters in the North Atlantic, carbonate deposition at the deep North Pacific core sites is enhanced during glacial periods, and occasionally higher than at shallow North Atlantic Site 552 even though Site 552 was probably above lysocline-depth during most of the late Pleistocene. This apparent paradox can be resolved only by invoking an increase in alkalinity in the glacial North Pacific which would have increased the degree of carbonate ion saturation and thereby improved the state of carbonate preservation.

1. Introduction

Variations in the ocean's carbonate system through time are of fundamental interest for chemical oceanography and paleoclimatology. Such variations affect the carbon dioxide buffer capacity of the ocean and have the potential of significantly enhancing fluctuations of atmospheric CO_2. Chemistry-oriented ocean–climate models call for enhanced carbonate dissolution and subsequent alkalinity readjustments [1–6] as one possible mechanism for reducing the CO_2 concentration in the glacial atmosphere. The sedimentary record obtained from Atlantic and Pacific Ocean core sites, however, suggests that carbonate deposition has varied between in-phase and out-of-phase fluctuations between both ocean basins during the late Pleistocene [7,8] implying that carbonate dissolution was not the same in the world ocean. These patterns have been broadly attributed to a redistribution of carbonate ions between both oceans induced by changing deep-water circulation. At the same time benthic foraminiferal $\delta^{13}C$ records obtained from Pacific and Atlantic sediment cores show a nearly coherent pattern, the Pacific $\delta^{13}C$ values being continuously lower by 1.0–1.5‰ than the Atlantic values [9,10] suggesting that the chemical asymmetry, and conceivably also the advective flow of deep

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waters between the Atlantic and Pacific, was reasonably stable during glacial–interglacial times. This apparent paradox points to some basic reorganization within the ocean's carbon cycle during glacial–interglacial times. We present new benthic isotope and carbonate records of two sediment cores from the deep subarctic Pacific. Comparison of the core profiles with similar records available from shallow North Atlantic DSDP Site 552 implies a nearly out-of-phase response of carbonate deposition to climatic change between the North Pacific and the North Atlantic. At the same time the interoceanic offset of benthic $\delta^{13}C$ between DSDP Site 552 and our North Pacific sites has remained nearly constant. Continuously low $\delta^{13}C$ values suggest that the concentration of ΣCO_2 derived from the oxidation of organic matter was higher in the North Pacific than in the North Atlantic during the past 750,000 years. Whereas this should have resulted in a continuously enhanced carbonate dissolution in the North Pacific, carbonate deposition there was higher during glacial times supporting the hypothesis that oceanic alkalinity was higher in the glacial ocean [4].

2. Analytical methods and results

2.1. *Stable isotope stratigraphy and sedimentation rates*

Stable isotope records were measured for North Pacific cores END77-29 (48°34′N, 133° 57′W; 3695 m) and Y70-5-64 (48° 25′N, 132° 46′W; 2944 m). Both cores were continuously sampled at 10 cm intervals. In addition, sub-samples were taken at 5 cm intervals for the upper two meters of core Y70-5-64 in order to improve the resolution of the stable isotope and carbonate stratigraphies of the last two climatic cycles. A higher sampling density is unlikely to have improved our stratigraphies since sedimentation rates at both core sites are low and fluctuations of carbonate and foraminiferal abundances are high. This makes the down-core records more susceptible to bioturbational smoothing than records from core sites where sedimentation rates are high (see below). The isotope measurements were run at Christian Albrechts University of Kiel (CAU) and at Oregon State University (OSU) on Finnigan MAT 251 mass spectrometers. Calibration of the mass spectrometers at CAU and OSU was done through National Institute of Standards and Technology "NBS" carbonate standards 19 and 20, and an internal working standard (Solenhofen Limestone, similar to NBS 20). External precision (including carbonate preparation and spectrometric analysis) for $\delta^{18}O$ and $\delta^{13}C$ at OSU is better than respectively 0.1‰ and 0.06‰, and better than respectively 0.07‰ and 0.04‰ at CAU. All isotope data are listed in Appendix A and B.

Isotope measurements were carried out mostly on benthic foraminifer *Cibicidoides wuellerstorfi*, some isotope data were measured on *Uvigerina* spp. (mostly (*U. peregrina* and *U. auberiana*). The oxygen isotope data are reported on the *Uvigerina* scale of $\delta^{18}O$ which is believed to be closest to

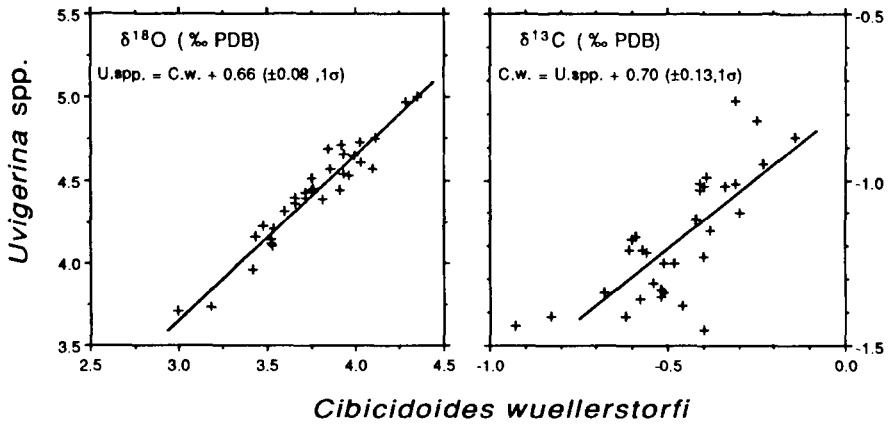

Fig. 1. 31 paired analyses of $\delta^{18}O$ and $\delta^{13}C$ from *C. wuellerstorfi* (*C.w.*) and *Uvigerina* spp. (*U.spp*). The carbon isotope difference of 0.7‰ has been used in this study as an interspecific conversion factor for $\delta^{13}C$.

isotope equilibrium as defined by temperature and oxygen isotope composition of the ambient water masses [11]. $\delta^{18}O$ data of *C. wuellerstorfi* were converted into equivalent values of *Uvigerina* by adding 0.64‰ which is a well-accepted conversion factor for both genera [11], and which is closely reproduced by our data (Fig. 1). Similarly, $\delta^{13}C$ data of *Uvigerina* were converted into equivalent values of *C. wuellerstorfi* which is believed to record the $\delta^{13}C$ signal of ambient water ΣCO_2 ([9] and references therein). This conversion appears to be justified because we have not observed any

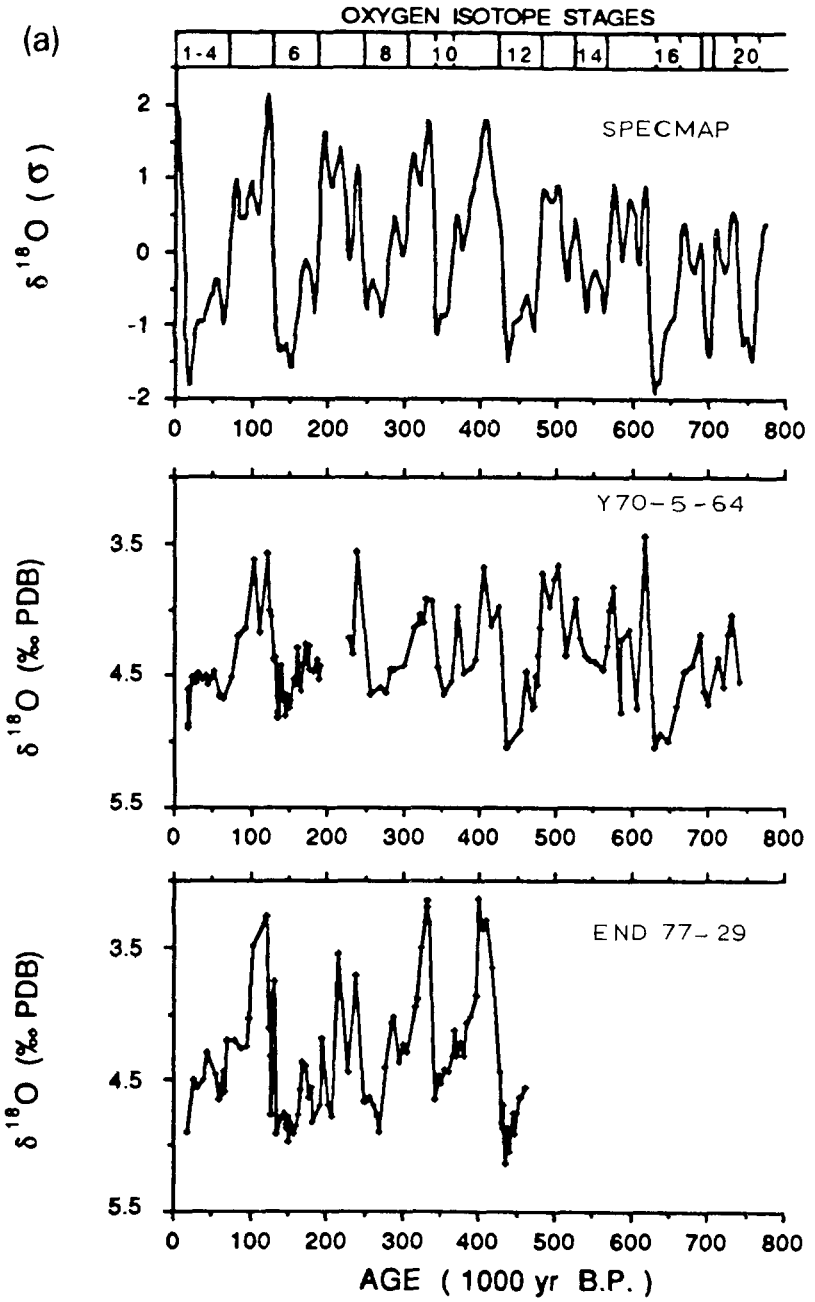

Fig. 2a. Oxygen isotope records of cores Y70-5-64 and END77-29 versus age. The Specmap global stack of $\delta^{18}O$ (top, from [15]) has been used as the time-scale reference.

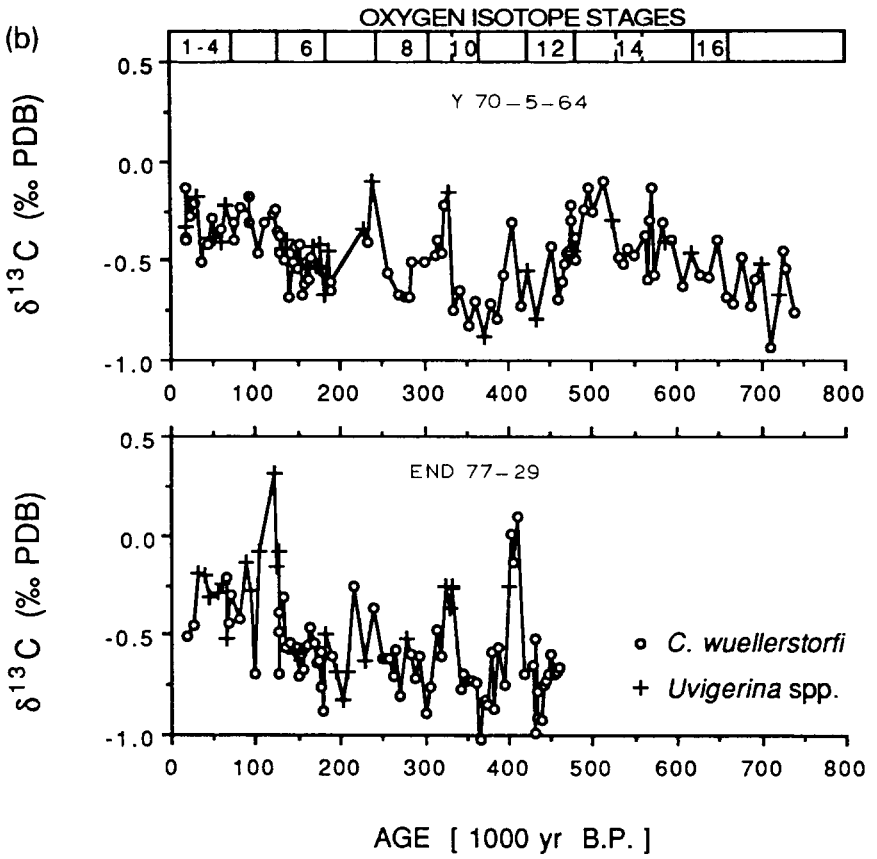

Fig. 2b. Carbon isotope records (*Cibicidoides* scale) of cores Y70-5-64 and END77-29 versus age.

systematic shifts of the interspecific $\delta^{13}C$ difference along the cores, and because biological productivity and the flux of organic matter to the sea floor is low in the subarctic North Pacific. Potential microhabitat effects [12–14] on the interspecific $\delta^{13}C$ fractionation between *Uvigerina* spp. and *C. wuellerstorfi* are therefore only a minor concern at our North Pacific core sites. In accordance with the interspecific $\delta^{13}C$ offset observed at our cores we use here a conversion value of 0.7‰ (Fig. 1).

The oxygen isotope records of cores Y70-5-64 and END77-29 show considerable scatter along the length of the cores (Fig. 2a). This is probably due to the combined effects of low sedimentation rates and high-amplitude variations of carbonate which allow for more severe distortion of the records than is usually encountered. Extremely low carbonate contents caused a data gap in core Y70-5-64 between 2.6 and 3.4 m. We believe that this core section represents interglacial stage 7. For core END77-29, some $\delta^{18}O$ measurements made on samples from the same isotope stage (i.e., between 2.3 and 3.0 m) still have glacial values. Isotope measurements for this core section were made on only 1 to 3 specimens per sample which may have been admixed into the stage 7 sediments through bioturbation from the high-carbonate glacial core sections above and below.

Chronostratigraphies for cores END77-29 and Y70-5-64 were developed by visually correlating the oxygen isotope records to the Specmap global stack of $\delta^{18}O$ [15]. Accordingly, core base ages of 460,000 and 750,000 years for cores END77-29 and Y70-5-64, respectively, have been obtained (Fig. 2a). The derived chronologies were then applied to the carbonate records of both cores. Fine-tuning of the time scales was done by graphi-

cally correlating their carbonate records. This tuning procedure was necessary because the $\delta^{18}O$ curve structure of some core sections was not conclusive as to the exact correlation with the Specmap reference $\delta^{18}O$ record, especially in the low-carbonate sections. The time models imply average sedimentation rates of respectively 1.3 and 1.6 cm 1000 yr^{-1} for cores END77-29 and Y70-5-64 (Fig. 3). Along the sediment cores sedimentation rates vary between 0.8 and 2.4 cm 1000 yr^{-1}. This yields a mean time resolution [calculated as the Nyquist period: $N = 2 \setminus F$(sample interval, sedimentation rate)] of the isotope and carbonate records between 8.3 and 25 kyr at sampling intervals of 10 cm. Some rate maxima correlate with climatic transitions, e.g., at stage boundaries 5/6 and 12/13 (Fig. 3), and coincide with massive fluxes of ice-rafted debris. Other maxima, e.g., during mid-stage 8, have resulted from our attempt to correlate the oxygen isotope records with the corresponding curve structure of the Specmap stack. These maxima may be due to inaccuracies and irregularities of our isotope records with respect to the Specmap stack.

The $\delta^{13}C$ records of cores Y70-5-64 and END77-29 (Fig. 2b) display increased values during interglacial times and more negative values during glacial times. Maximum shifts of about 1‰ are observed in core END77-29 at stage boundaries 12/11 and 6/5. In both cases the $\delta^{13}C$ values in this core are increased by 0.5‰ compared to those of core Y70-5-64 pointing to possible distortions by bioturbation. Both records show a long-term trend towards an apparent mid-Brunhes $\delta^{13}C$ minimum at approximately 360,000 yr B.P. The stratigraphic resolution of the $\delta^{13}C$ records does not allow for more specific estimates as to potential phase shifts relative to $\delta^{13}C$ records obtained from other parts of the world ocean. However, the results to date suggest that the $\delta^{13}C$ records from our North Pacific core sites follow the general trend observed for the deep ocean where glacial $\delta^{13}C$ values are more negative than interglacial $\delta^{13}C$ values. In this regard, the data confirm the

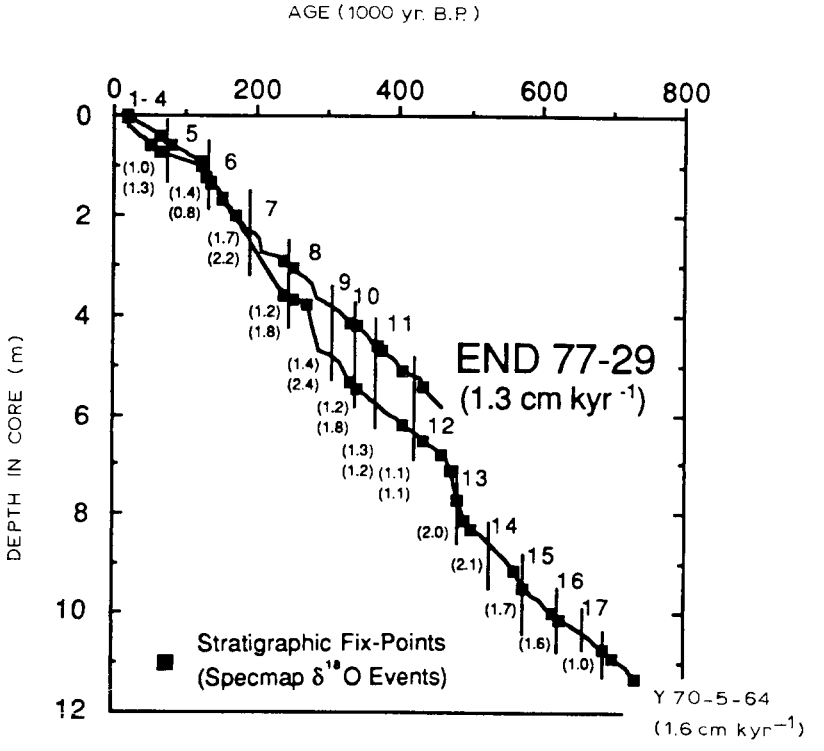

Fig. 3. Age–depth relationships for cores END 77-29 and Y 70-5-64. Oxygen isotope stages are given on top of the age–depth curves, mean sedimentation rates for each stage are given below the curves (values for core Y 70-5-64 below those for core END 77-29). Squares mark position of chronostratigraphic fix-points.

hypothesis [16] that the glacial–interglacial carbon isotope history of deep-water ΣCO_2 in the subarctic North Pacific was not much different from that of the world ocean.

2.2. *Carbonate records*

Carbonate analyses for core Y70-5-64 were run at OSU using a Leco carbon analyzer following the analytical procedure described in [17]. The average daily reproducibility of carbonate standards was better than 0.6% (1 σ). Accuracy of this system was better than 1.5% as obtained from 41 replicate carbonate standard measurements and from 20 reruns of sediment samples over a period of 9 months. Carbonate contents for core END77-29 were determined at the Pacific Geoscience Centre (PGC) by weight loss after stripping the samples with hydrochloric acid. Average reproducibility of this method was better than 0.6% (1 σ) based on eight replicate sample measurements. The carbonate records of cores Y70-5-64 and END77-29 are similar in structure and amplitude (Fig. 4a). Yet the carbonate minima in the shallower core Y70-5-64 (2944 m) are close to 0% whereas carbonate values at the deeper site END77-29 (3695 m) do not fall below 10%. This may point to a systematic offset between the two analytical procedures employed here. However, since these are the first carbonate records available from this area we do not know what the true glacial–interglacial carbonate levels are and thus, we did not correct either record for potential analytical offsets. In the later discussion we will focus on the amplitude of variation rather than on absolute carbonate values.

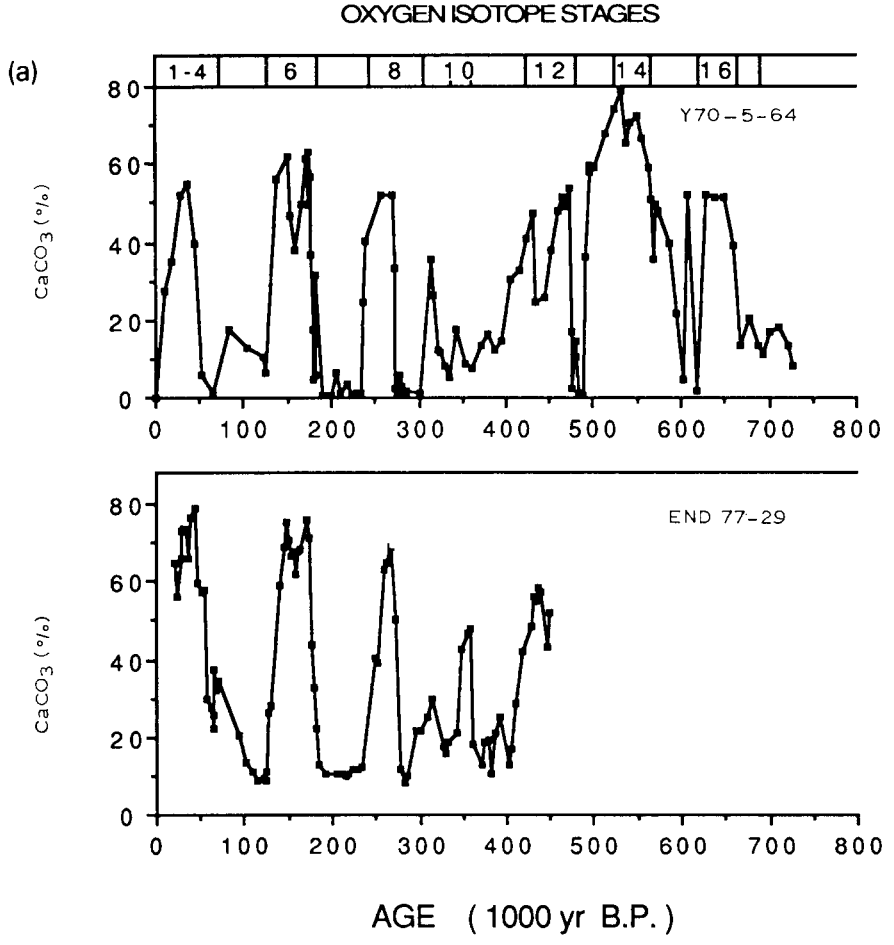

Fig. 4a. Carbonate records (weight %) of cores Y70-5-64 and END77-29 versus age.

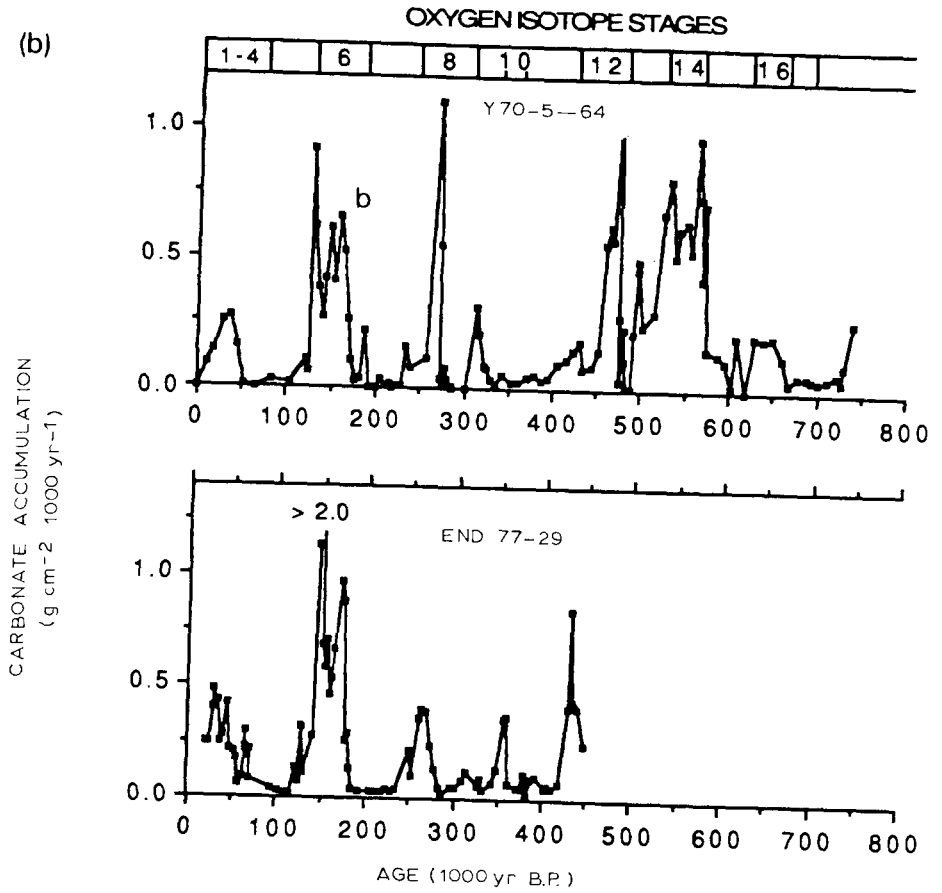

Fig. 4b. Records of carbonate accumulation for cores Y70-5-64 and END77-29. Percent carbonate has been converted into rates of carbonate accumulation using an empirical relationship between carbonate content and dry bulk density, and by using the sedimentation rates as derived from the time stratigraphies. For discussion see text.

The carbonate records of cores Y70-5-64 and END77-29 show large-scale fluctuations by up to 70% (Fig. 4a). Both records display the standard Pacific carbonate cycles with enhanced values during glacial times and decreased values during interglacial times [8,18–23]. Prior to 400,000 yr B.P. the profile of core Y70-5-64 shows a gradual increase of $CaCO_3$ to the whole-core maximum with values close to 80% during isotope stages 13 and 14. This maximum is followed by a broad minimum between 300,000 and 400,000 years B.P., and the carbonate records thus follow the long-term Brunhes pattern of carbonate deposition observed e.g., in the equatorial Pacific [24].

Fluctuations of percent carbonate are a function of carbonate production in the surface ocean, dilution with non-carbonate material, and carbonate dissolution. In order to eliminate the possible effects of dilution we have converted the records of $CaCO_3$ content (weight %) into profiles of $CaCO_3$ accumulation (g cm^{-2} 1000 yr^{-1}) (Fig. 4b). The conversion was made using the empirical relationship given in [25] which relates dry bulk density to the carbonate content of the sediments. Accumulation rates were then calculated as the product of sedimentation rate, percent carbonate and estimated dry bulk density. The empirical equation of [25] was derived from sediment data of the equatorial Pacific where the non-carbonate fraction consists mostly of diatomaceous opal. However, opal has a lower density than ice-rafted debris which is the most important non-carbonate component in the subarctic North Pacific and thus, using the equation of [25] we have probably underestimated the density of the non-carbonate fraction at our high-latitude core sites. Given these

constraints the variations of carbonate accumulation may have been slightly less than those shown in Fig. 4b.

3. Atlantic-Pacific chemical fractionation: the sedimentary record

Spatial variations of the lysocline and the Carbonate Compensation Depth (CCD) are closely tied to the ocean's circulation pattern. Detailed records of benthic foraminiferal $\delta^{13}C$ and Cd/Ca ratios as well as paired planktonic-benthic ^{14}C data indicate that the chemical fractionation and conceivably also the advective flow of deep waters between the Atlantic and the Pacific has been reasonably stable during the late Pleistocene [26–30]. Comparison of sedimentary records of core sites from both oceans has further revealed that fluctuations of carbonate deposition have not been the same for both oceans, the differences being attributed to changes of formation rates of North Atlantic Deep Water [8,29]. We have chosen the stable isotope and carbonate record of North Atlantic DSDP Site 552 (56° N, 23° W; 2.3 km) as a reference for comparison to our North Pacific records. We have chosen this northern, shallow core site over other, deeper Atlantic core sites because it is close to the source of Atlantic deep waters also during glacial times, and because it has probably remained above lysocline-depth during most of the late Pleistocene. That is, DSDP Site 552 and our subarctic North Pacific core sites

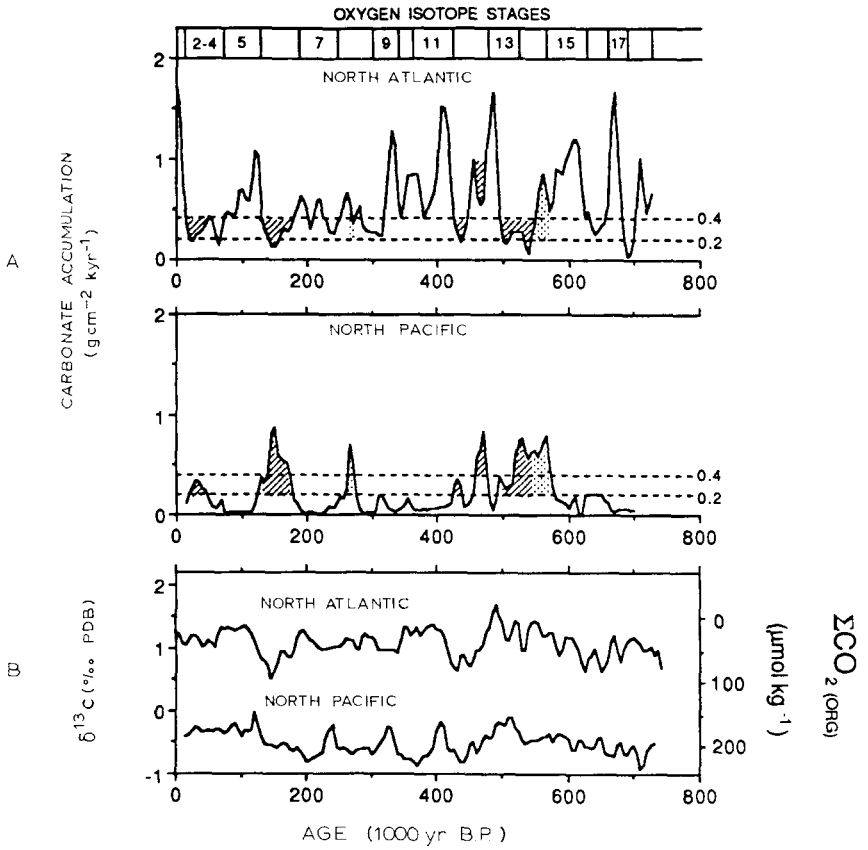

Fig. 5. Comparison of carbonate and $\delta^{13}C$ records from North Atlantic DSDP Site 552 and our North Pacific core sites. The North Pacific records are the mean between the records of cores END 77-29 and Y 70-5-64; all records are smoothed with a 15-kyr Gaussian filter at an effective step size of 5 kyr. (A) Carbonate accumulation. Shading shows sections where carbonate accumulation in the North Pacific is similar to (stippled sections) or higher than (diagonal ruling) at shallow North Atlantic DSDP Site 552. Phase estimates for the time intervals 0–200 kyr B.P. and 400–600 kyr B.P., where the coherency between the Atlantic and Pacific carbonate records is high, are 155° ±25° (80% confidence level) in the frequency bands equivalent to the 41kyr and 100-kyr periods. (B) Benthic $\delta^{13}C$ records. Right hand axis is an estimated scale for $\Sigma CO_{2(org)}$. For discussion see text.

are at the opposite ends of the deep-water pathway from the North Atlantic to the North Pacific, and also of the oceanic carbonate cycle. Percent carbonate data and benthic isotope profiles from Site 552 were available from Zimmermann et al. [30] and Shackleton and Hall [31]. The percent carbonate record was converted into a profile of carbonate accumulation following the same conversion procedure as described in section 2.2 using the time stratigraphy given in [31].

As Fig. 5A shows, carbonate deposition is nearly out of phase between the North Atlantic and the North Pacific during most of the late Pleistocene, the deep-Pacific values being higher than those documented at shallow, North Atlantic Site 552 during oxygen isotope stages 2, 6, 10, 13 and 14. At the same time benthic foraminiferal $\delta^{13}C$ values at our North Pacific core sites consistently remain more negative than those obtained at North Atlantic DSDP Site 552 (Fig. 5B). As we will show below, the combined pattern of carbonate and benthic $\delta^{13}C$ variation suggests major vertical migrations of the North Pacific lysocline in response to the ocean's alkalinity cycle, whereas the North Atlantic lysocline at Site 552 remained reasonably stable at its modern depth position during the past 750,000 years.

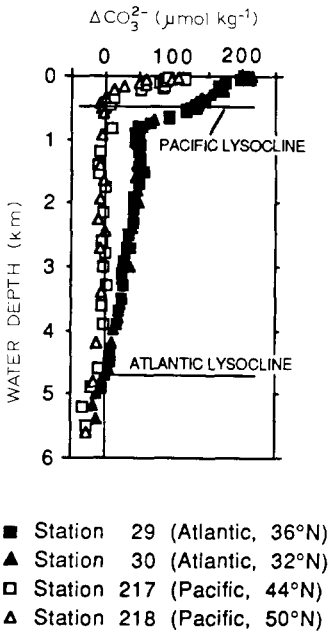

Fig. 6. Vertical sections of carbonate ion saturation (ΔCO_3^{2-}) calculated from hydrographic profiles at Geosecs stations in the North Atlantic and the North Pacific. The ΔCO_3^{2-} profiles have been computed using the equations of [34,35]. Also shown are the depth positions of the regional sedimentary lysoclines as defined in [34].

4. Carbonate dissolution: controls and proxies

The distribution of $CaCO_3$ in deep sea sediments is controlled by the flux of $CaCO_3$ to the seafloor and by the degree of carbonate ion saturation in seawater. We use the carbonate dissolution model of Broecker and Peng [32] to determine the effect of varying degrees of carbonate undersaturation on the rate of carbonate dissolution in the North Atlantic and the North Pacific. The model determines percent carbonate at depth (f) and rates of carbonate dissolution as a function of the degree of carbonate saturation of seawater (ΔCO_3^{2-}), the rain rate (R) and the fraction of carbonate (F_L) of the particle flux leaving the sea surface:

$$\Delta CO_3^{2-} \sqrt{\frac{Dsf}{\tau}} = R\left[1 - \frac{f(1-F_L)}{F_L(1-f)}\right] \quad (1)$$

where ΔCO_3^{2-} is the difference between estimated $[CO_3^{2-}]$ (saturation) and measured $[CO_3^{2-}]$(*in situ*); τ is the pore water resaturation time (set here to 90 s) and Ds is the carbonate ion diffusion coefficient (set here to 4×10^{-6} cm^2 s^{-1}). Modern input rates of carbonate to the North Pacific and the North Atlantic have been set to 1 g cm^{-2} kyr^{-1} and 1.8 g cm^{-2} kyr^{-1}, respectively. These values have been estimated from the Holocene carbonate record of Site 552 and from sediment traps deployed in the North Pacific [33]. The sediment traps and Site 552 are above the regional lysoclines in the North Pacific and the North Atlantic and we assume that the carbonate fraction of the respective samples has not been affected by dissolution thus allowing the use of the estimated carbonate fluxes as modern values for F_L. The carbonate ion saturation (ΔCO_3^{2-}) of the North Atlantic and North Pacific deep waters was determined using *in situ* data from Geosecs Stations 29 and 30 (North Atlantic), and 217 and 218 (North Pacific) which were nearest to the core sites. Vertical profiles of carbonate saturation (Fig. 6) were determined using the equations given in Broecker and Takahashi [34] and by estimating

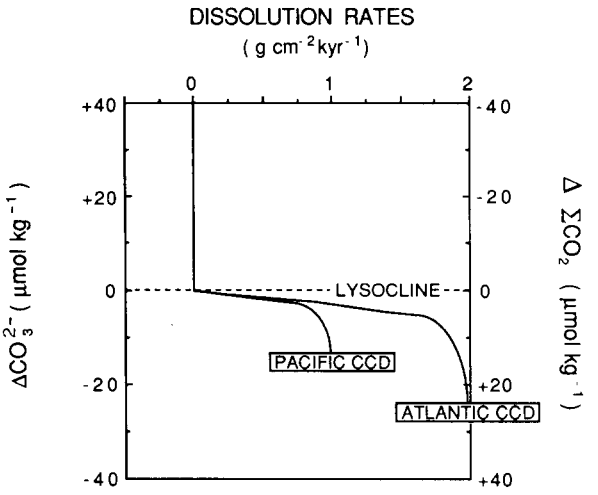

Fig. 7. Plot of calcite dissolution rate as a function of carbonate ion saturation (ΔCO_3^{2-}) of seawater. Dissolution rates have been calculated after equation (1) and by using the ΔCO_3^{2-} profiles shown in Fig. 6. Carbonate flux to the seafloor was set to 1 and 1.8 g cm^{-2} kyr^{-1} for the North Pacific and North Atlantic Oceans, respectively. For discussion see text.

the solubility product of calcite using the equation of Plath et al. [35]. All titrimetric ΣCO_2 values of the Pacific Geosecs stations have been corrected by -15 μmol kg^{-1} so as to compensate for a systematic overestimation due to incomplete data reduction by the original computation scheme [34].

As Fig. 7 shows, the carbonate dissolution model predicts rapidly increasing rates of carbonate dissolution at increasing concentrations of ΣCO_2 which in turn decrease the degree of carbonate ion saturation. The CCD being defined as the horizon where the rate of dissolution exceeds the rate of $CaCO_3$ accumulation is reached in the North Atlantic and North Pacific at ΔCO_3^{2-} values of -25 and -15 μmol kg^{-1}, respectively (Fig. 7). These degrees of undersaturation are reached at water depths just below 4 km in the North Pacific and below 5 km in the North Atlantic (Fig. 6) which is in good agreement with the regional depth positions of the foraminiferal CCD in both ocean basins [36].

The continued input and oxidation of marine organic matter results in a progressive lowering of $\delta^{13}C_{\Sigma CO_2}$ and a progressive increase of ΣCO_2 as the deep-ocean water masses flow away from their sites of convection. The covariance between the concentration of ΣCO_2 and $\delta^{13}C_{\Sigma CO_2}$ in the deep ocean is described by the empirical regression equation [37]:

$$\delta^{13}C_{\Sigma CO_2} = \delta^{13}C_{(preformed)} - a \cdot AOU \qquad (2)$$

where $\delta^{13}C_{(preformed)}$ is the carbon isotope composition of dissolved ΣCO_2 in the surface waters by the time convection occurs, AOU is the Apparent Oxygen Utilization given in units of μmol kg^{-1} and a is the slope of the equation which defines the AOU gain per unit of $\delta^{13}C_{\Sigma CO_2}$ decrease and which is a function of the carbon isotope composition of the oxidizable carbon fraction. In the modern ocean, $\delta^{13}C_{(preformed)}$ and slope a are respectively + 1.5‰ (PDB) and 0.0075 [37].

Using the benthic $\delta^{13}C$ records of our North Pacific sediment cores and of Site 552 as a proxy for $\delta^{13}C_{\Sigma CO_2}$ we have applied equation (2) to estimate the amount of oxygen utilized by the oxidation of organic matter at the North Atlantic and North Pacific core sites. AOU has then been transformed into units of $\Sigma CO_{2(org)}$ assuming a constant ratio of 1 : 1.3 between carbon release and oxygen consumption during oxidation of organic matter. As Fig. 5B shows, the benthic $\delta^{13}C$ records imply that $\Sigma CO_{2(org)}$ concentrations in deep waters of the North Pacific were continuously higher by some 160 μmol kg^{-1} than in the North Atlantic.

An apparent limitation of our ΣCO_2 estimates arises from the fact that $\delta^{13}C_{\Sigma CO_2}$ is determined by the oxidation or organic matter and that the spatial distribution of $\delta^{13}C$ of the oceanic carbon fraction remains largely unaffected by the $\delta^{13}C$ of the inorganic carbon fraction which is released during the dissolution of carbonate. Also, $\delta^{13}C_{(preformed)}$ and the carbon isotope composition of the oxidizable carbon fraction in the ocean may have systematically changed during glacial–interglacial times [9,10,38–40]. A sensitivity test of equation (2) (Fig. 8) shows that a reduction of $\delta^{13}C_{(preformed)}$ and of $\delta^{13}C$ of the oxidizable carbon fraction in the ocean from modern values of respectively +1.5‰ and −20‰ (PDB) to glacial values of respectively +0.5‰ and −30‰ (PDB) would reduce the $\Sigma CO_{2(org)}$ gain per unit $\delta^{13}C_{\Sigma CO_2}$ depletion by about 30%. That is, the interoceanic offset of $\Sigma CO_{2(org)}$ between the North Atlantic and the subarctic North Pacific as inferred from benthic $\delta^{13}C$ (Fig. 5B) could have been reduced to 110 μmol kg^{-1}, if during glacial times the mean

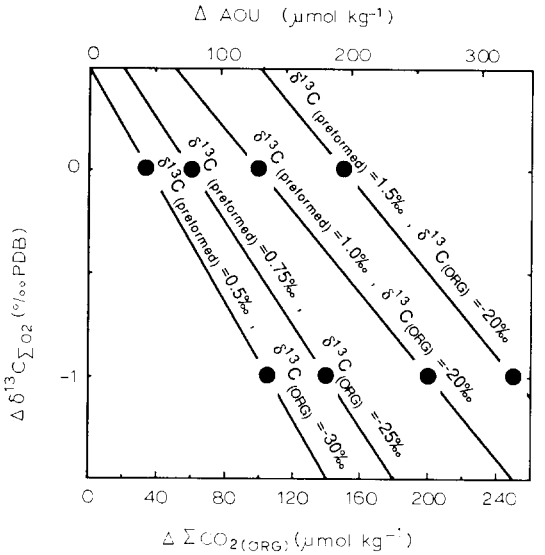

Fig. 8. Sensitivity test of the $\delta^{13}C$–AOU relationship to varying $\delta^{13}C$ of the oxidizable carbon fraction in the oceans. If all marine organic carbon ($\delta^{13}C \approx -20‰$ PDB) would be replaced by terrestrial organic carbon ($\delta^{13}C \approx -30‰$ PDB), this would reduce the gain of AOU (and thus of ΣCO_2) per unit $\delta^{13}C$ decrease by about 30%.

carbon isotope composition of the oxidizable carbon fraction in the ocean has changed from a predominantly marine value of approximately −20‰ (PDB) to a predominantly terrestrial value of close to −30‰ (PDB). However, because such changes would have affected the world ocean uniformly and synchronously, the interoceanic gradient of benthic $\delta^{13}C$ would still support the contention that deep waters in the North Pacific were continually enriched with $\Sigma CO_{2(org)}$ relative to those of the North Atlantic.

5. Pleistocene carbonate preservation and benthic $\delta^{13}C$: geochemical implications

It has long been the consensus of paleoceanographers that carbonate preservation was enhanced in the Pacific during glacial intervals (7,24,25,41]. At the same time carbonate dissolution in the deep Atlantic would have intensified during glacial periods due to decreased deep-water ventilation thus resulting in a dissolution pattern opposite to that of the Pacific [7,8,42]. Reduced ventilation of the Atlantic during glacial times would have increased the ΣCO_2 in Atlantic deep waters and thereby lowered the carbonate ion concentration and enhanced carbonate dissolution.

Whereas this concept appears to be consistent with the reduced rates of carbonate deposition and low benthic $\delta^{13}C$ values recorded in glacial sections from deep-Atlantic core sites, it cannot explain the combined $CaCO_3$-$\delta^{13}C$ signal at our North Pacific core sites. The apparent paradox between continuously low $\delta^{13}C$ and enhanced carbonate deposition can be resolved only by invoking an increase of alkalinity in the glacial North Pacific which would have increased $[CO_3^{2-}]$ and thus also the state of carbonate preservation (Fig. 9). Ambient deep waters at shallow North Atlantic DSDP Site 552 are today supersaturated with carbonate ions (Figs. 6 and 9) and Site 552 has probably remained above lysocline-depth during most of the late Pleistocene. The fact that carbonate accumulation in the deep North Pacific

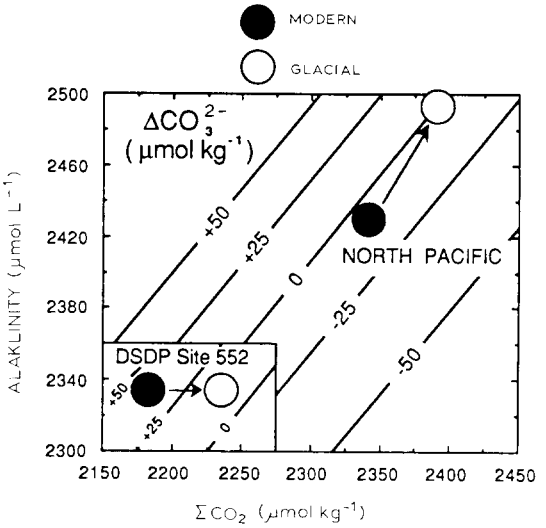

Fig. 9. ΣCO_2—alkalinity diagram showing isolines of carbonate ion saturation (ΔCO_3^{2-}, i.e. $[CO_3^{2-}]$(*in situ*) minus $[CO_3^{2-}]_{(saturation)}$). A shift towards carbonate ion saturation in the deep North Pacific at increased glacial concentrations of ΣCO_2 could have been achieved only if seawater alkalinity has simultaneously been increased. $[CO_3^{2-}]$ at North Atlantic DSDP Site 552 would have remained above the saturation level during glacial times. Modern ΔCO_3^{2-} has been computed using *in situ* hydrographies at DSDP Site 552 ($Z = 2.3$ km: $T = 3.6\,°C$, $S = 34.98$, $\Sigma CO_2 = 2182$ μmol kg^{-1}, Alk = 2334 μmol L^{-1}) and of North Pacific Geosecs stations 217 and 218 ($Z = 3.0$–3.7 km: $T = 1.5\,°C$, $S = 34.67$, $\Sigma CO_2 = 2338$ μmol kg^{-1}, Alk = 2430 μmol L^{-1}). Glacial ΔCO_3^{2-} has been estimated setting $T = 0\,°C$ and increasing salinities and ΣCO_2 by 1 and 50 μmol kg^{-1}, respectively, to accommodate glacial-ocean boundary conditions.

during glacial times was similar to or even higher than in the shallow North Atlantic provides distinct evidence for major vertical fluctuations of the North Pacific lysocline.

Applying thermodynamic relationships in the oceanic carbonate system [34], we can estimate the change in $[CO_3^{2-}]$ needed to bring the carbonate system at our core sites close to saturation by using Geosecs measurements of ΣCO_2 and Alk for the modern ocean. $[CO_3^{2-}]$ at North Pacific Geosecs stations 217 and 218 between 3.0 and 3.7 km water depth is about 62 μmol kg^{-1}, which is 7 μmol kg^{-1} below the saturation level (i.e., $\Delta CO_3^{2-} = -7$ μmol kg^{-1}, Figs. 6 and 9). Assuming that equation (2) applies for the glacial ocean, we infer from benthic foraminiferal $\delta^{13}C$ that glacial ΣCO_2 was 50 μmol kg^{-1} higher, i.e., 2388 μmol kg^{-1} compared to 2338 μmol kg^{-1} today. If these values apply for our core sites, glacial $[CO_3^{2-}]$ at these sites would have to be 23 μmol kg^{-1} higher than today to be near the lysocline (i.e., $\Delta CO_3^{2-} = 0$ μmol kg^{-1}). For $[CO_3^{2-}]$ to have increased by 23 μmol kg^{-1}, Alk would have to have increased by about 64 μmol l^{-1} (Fig. 9). At DSDP Site 552 a glacial ΣCO_2 increase of 50 μmol kg^{-1} would have decreased the carbonate ion saturation to a

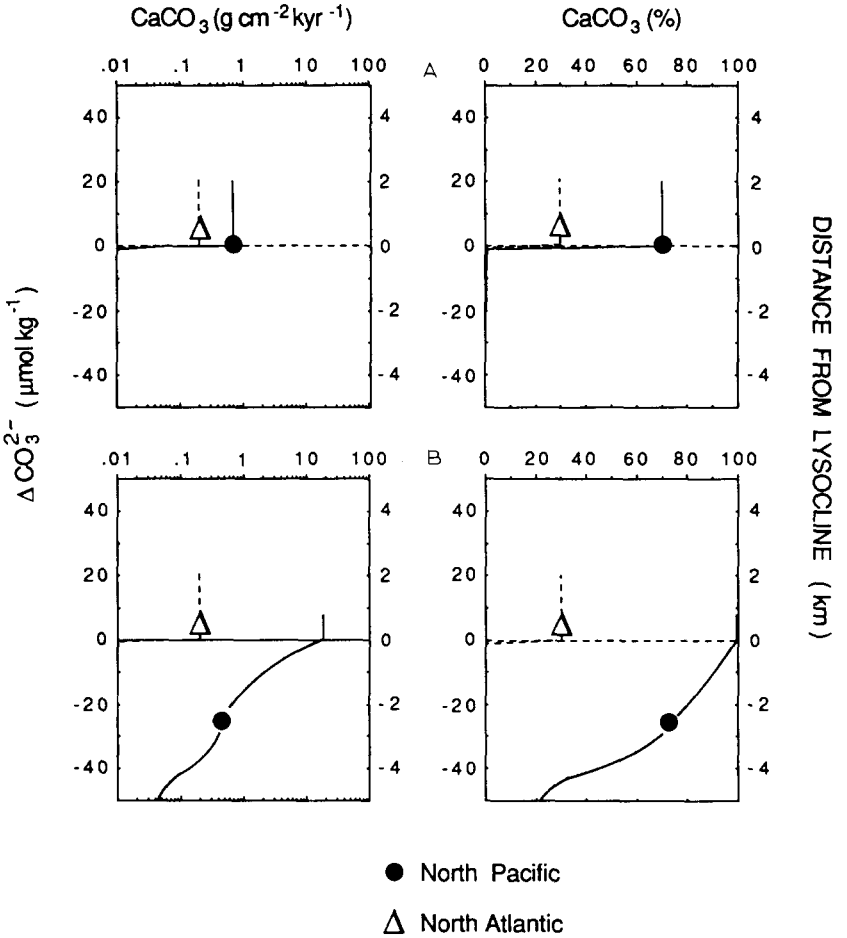

Fig. 10. Simulated depth profiles of carbonate accumulation and percent carbonate for the glacial North Pacific (full dot, solid lines) and North Atlantic (open triangle, dashed lines). The profiles were computed using equation (1). Symbols depict depth position below the lysocline and mean glacial carbonate values of the sediment cores. (a) Vertical carbonate distribution if the sedimentary lysocline was close to the core sites in the North Pacific and if the enhanced carbonate deposition was primarily due to an enhanced state of carbonate saturation of seawater. (b) Vertical carbonate distribution if the gradients of carbonate saturation in the glacial North Pacific were similar to the modern and if the glacially enhanced carbonate deposition was primarily due to an increase of the carbonate flux. Modern depth position of the North Pacific cores in the diagrams would be about 2.5 km below the lysocline.

ΔCO_3^{2-} value of $+11$ μmol kg^{-1}, compared to $+40$ μmol kg^{-1} today (Fig. 9). That is, glacial $[CO_3^{2-}]$ would still have been above the saturation level and glacial–interglacial carbonate fluctuations at Site 552 would have most likely resulted from a lower, glacial-stage carbonate productivity.

This glacial carbonate preservation scenario is schematically illustrated in Fig. 10a. For comparison, if the observed pattern of carbonated deposition in the North Pacific were to be explained solely as a function of carbonate productivity, an increase of carbonate input and carbonate productivity in the North Pacific from modern values of respectively 70% and 1 g cm^{-2} kyr^{-1} to glacial-maximum values of close to respectively 100% and 20 g cm^{-2} kyr^{-1} would be required (Fig. 10b). This is unlikely and a change in carbonate preservation appears to be more realistic. If $[CO_3^{2-}]$ at our North Pacific core sites at about 3 km water depth was indeed close to saturation during the late Pleistocene glacial periods, this would imply that the lysocline in the subarctic North Pacific had dropped from an interglacial (= modern) depth position of about 500 m to almost 3 km during glacial times. This vertical shift of the lysocline would have been much larger than that estimated for the equatorial Pacific and the Atlantic where Pleistocene depth variations of the lysocline are believed to be less than 700 m [24,41]. If so, this would imply that chemical reorganizations in the ocean during global climatic change [4,6] were largest in the North Pacific.

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APPENDIX A

Stable isotope data for core END 77-29

Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*		Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*	
		$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$			$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$
0.00	18.00			4.26	−0.51	3.04	248.80			4.01	−0.62
0.06	26.00			3.85	−0.45	3.09	251.00			4.01	−0.62
0.12	31.00	4.55	−0.89			3.13	257.50			3.98	−0.62
0.19	38.00	4.49	−0.90			3.18	261.67			4.04	−0.70
0.23	45.00	4.28	−1.01			3.23	265.80			4.13	−0.57
0.31	55.00	4.45	−0.99			3.28	270.00	5.46	−0.99	3.67	−0.80
0.34	60.00	4.64	−0.94			3.36	277.50	4.40	−1.22		
0.37	63.90			3.80	−0.21	3.64	284.00			3.43	−0.60
0.42	65.00	4.60	−1.22			3.69	288.00			3.38	−0.71
0.47	68.00	4.58	−1.06	3.94	−0.44	3.74	294.00			3.72	−0.61
0.53	71.00			3.56	−0.30	3.79	300.00			3.59	−0.89
0.59	80.00			3.56	−0.42	3.83	306.38			3.65	−0.76
0.65	88.00	4.26	−0.84			3.92	315.00			3.31	−0.47
0.70	94.50	4.24	−0.98			3.96	319.31			3.25	−0.61
0.73	99.62	3.98	−0.88	3.43	−0.69	4.04	323.62	3.50	−0.95		
0.76	102.73	3.49	−0.78			4.13	331.00	3.15	−1.06		
0.93	122.00	3.26	−0.39			4.17	332.34	3.19	−0.95		
1.10	124.06	4.11	−0.86			4.21	333.68	3.31	−0.97		
1.15	126.12	3.94	−0.78			4.25	342.00			4.00	−0.77
1.17	127.06	4.77	−1.33	4.11	−0.69	4.30	346.50			3.82	−0.69
1.20	127.53			3.67	−0.48	4.34	350.00			3.88	−0.73
1.25	128.00	3.85	−0.92	3.43	−0.39	4.38	355.00			3.78	−0.73
1.30	131.50			3.12	−0.31	4.50	361.00			3.79	−0.74
1.36	135.00			4.27	−0.56	4.55	364.00			3.68	−1.07
1.41	140.50			4.15	−0.54	4.60	368.00			3.48	−0.84
1.47	146.00	4.75	−1.29			4.65	371.50			3.68	−0.83
1.54	147.31			4.19	−0.58	4.70	375.00			3.57	−0.85
1.58	148.62	4.81	−1.20	4.27	−0.56	4.75	380.00			3.67	−0.58
1.64	149.81			4.13	−0.70	4.80	382.50			3.42	−0.87
1.68	151.00			4.33	−0.59	4.85	388.00			3.38	−0.56
1.71	153.97			4.18	−0.60	4.95	395.00			3.22	−0.75
1.74	155.46			4.26	−0.67	5.00	399.00	3.13	−0.96		
1.77	156.94			4.27	−0.57	5.05	402.67	3.36	−0.63	2.72	0.01
1.82	159.60			4.21	−0.56	5.10	406.33	3.32	−0.64	2.73	−0.14
1.86	162.25			4.12	−0.55	5.15	410.00			2.65	0.09
1.90	164.91			3.93	−0.46	5.20	417.89	3.23	−0.79	3.42	−0.69
1.95	167.56			3.72	−0.54	5.25	428.00			3.80	−0.65
2.00	170.39			3.76	−0.64	5.30	430.33			4.18	−0.99
2.05	173.22			3.75	−0.63	5.35	431.56			4.05	−0.52
2.10	175.33			3.99	−0.76	5.40	432.78			4.22	−0.78
2.15	177.44	4.55	−1.15	3.90	−0.58	5.45	435.00			4.49	−0.91
2.19	180.22			3.91	−0.88	5.50	438.13			4.22	−0.92
2.27	182.00	4.82	−1.20			5.55	441.25			4.40	−0.75
2.32	190.35			4.05	−0.61	5.60	444.38			4.10	−0.73
2.37	195.00	4.18	−1.38			5.65	447.50			4.27	−0.69
2.48	203.00	4.68	−1.52			5.70	450.63	4.77	−1.16	4.07	−0.59
2.72	207.00	4.78	−1.38			5.75	453.75			3.99	−0.69
2.78	216.00			2.90	−0.25	5.80	456.88			3.99	−0.68
2.85	228.00	4.44	−1.33			5.85	460.00	4.66	−1.15	3.80	−0.66
2.92	238.00	3.71	−0.78	3.31	−0.37						

APPENDIX B

Stable isotope data (‰ PDB) for Core Y 70-5-64

Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*		Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*	
		$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$			$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$
0.05	18.00	4.86	−1.03			4.71	287.00			3.81	−0.51
0.11	18.40	4.18	−0.92	3.96	−0.39	4.81	300.50	4.38	−1.34	3.81	−0.51
0.15	18.60			4.23	−0.40	4.91	314.00	4.32	−1.45	3.31	−0.47
0.21	19.00			4.26	−0.14	5.01	317.78	4.16	−1.45	3.43	−0.40
0.25	23.25	4.60	−0.71	3.78	−0.28	5.11	321.56	3.84	−1.11	3.59	−0.46
0.31	27.50	4.56	−0.87	3.90	−0.21	5.21	325.33	3.99	−1.25	3.56	−0.22
0.36	31.75	4.48	−0.88			5.31	329.11	3.92	−0.86		
0.41	36.00	4.35	−0.95	4.06	−0.51	5.41	335.33	3.89	−1.04	3.33	−0.75
0.46	40.25	4.44	−1.03	3.91	−0.41	5.51	344.00	4.23	−1.20	3.99	−0.65
0.51	44.50	4.53	−1.12	3.96	−0.42	5.61	352.71	4.61	−1.41	4.03	−0.83
0.56	48.75			3.87	−0.29	5.71	361.43	4.37	−1.39	4.06	−0.70
0.61	53.00	4.47	−1.09			5.81	370.14	3.97	−1.58		
0.65	59.00	4.65	−1.02	3.99	−0.34	5.91	378.86			3.84	−0.72
0.65	59.00	4.65	−1.11			6.01	387.57	4.62	−1.33	3.62	−0.79
0.71	65.00	4.67	−0.92			6.09	394.54	4.39	−1.21	3.72	−0.57
0.76	74.50	4.70	−0.87	3.62	−0.31	6.21	405.00	3.10	−0.55	3.62	−0.31
0.76	74.50			3.72	−0.40	6.31	414.67			3.48	−0.73
0.81	84.00	4.21	−0.95	3.54	−0.23	6.41	424.33	3.98	−1.25		
0.86	93.50	4.10	−1.01	3.53	−0.31	6.51	434.00	5.04	−1.49		
0.86	93.50			3.56	−0.18	6.71	452.00			4.27	−0.43
0.91	103.00	3.62	−1.06	3.52	−0.46	6.81	461.00			3.83	−0.69
0.96	112.50	4.22	−0.76	3.48	−0.31	6.91	464.33	4.69	−1.21	3.84	−0.61
1.01	122.00	3.57	−1.19	3.53	−0.27	7.01	467.67	4.57	−1.35	4.10	−0.52
1.05	123.78	4.05	−0.78	3.33	−0.24	7.11	471.00	4.73	−1.38	4.02	−0.46
1.11	126.46	3.98	−0.79	3.48	−0.35	7.21	472.67	4.43	−1.42	3.91	−0.45
1.17	129.14	4.59	−1.05	3.53	−0.38	7.31	474.33	4.43	−1.39	3.94	−0.30
1.21	130.92	4.49	−1.17	3.59	−0.46	7.41	476.00			3.93	−0.22
1.27	133.60	4.78	−1.14			7.51	477.67	4.34	−1.15		
1.31	135.38	4.43	−1.17	4.18	−0.50	7.61	479.33	4.12	−0.99	3.52	−0.39
1.37	138.06	4.69	−1.10			7.71	481.00	3.95	−0.85	3.09	−0.50
1.41	139.85	4.44	−1.34	3.75	−0.68	8.11	491.00	3.75	−0.80	3.34	−0.24
1.51	144.31	4.50	−1.43	4.16	−0.51	8.21	496.50	3.73	−0.87	3.18	−0.14
1.61	148.77	4.41	−1.37	4.00	−0.43	8.31	502.00	3.71	−0.82	2.99	−0.25
1.66	151.00	4.75	−1.31	4.11	−0.54	8.41	513.00	4.35	−0.66	3.38	−0.10
1.71	153.23	4.49	−1.34	4.04	−0.42	8.51	525.00	3.92	−1.00		
1.76	155.46			3.89	−0.67	8.61	531.33	4.24	−0.96	3.54	−0.49
1.81	157.69	4.57	−1.41	3.86	−0.62	8.71	537.67	4.39	−1.33	3.66	−0.52
1.86	159.92	4.28	−1.24			8.81	544.00	3.57	−1.11	3.74	−0.44
1.91	162.15	4.54	−1.25	3.93	−0.51	8.91	550.33	4.63	−1.15	3.50	−0.47
1.95	163.94			3.86	−0.59	9.11	563.00	4.51	−1.15	3.75	−0.38
2.01	166.62	4.32	−1.11	3.97	−0.48	9.21	565.75	4.31	−1.18	3.60	−0.60
2.05	168.40	4.41	−1.13			9.31	568.50	3.96	−1.10	3.42	−0.30
2.11	171.08	4.26	−1.23			9.41	571.25	3.90	−1.03	3.35	−0.13
2.15	172.86	4.40	−1.23			9.51	574.00	3.73	−0.92	3.28	−0.57
2.21	175.54	4.27	−1.24			9.60	585.00			4.13	−0.31
2.24	176.88	4.45	−1.11			9.61	586.00	4.23	−1.11		
2.34	181.34	4.47	−1.37			9.71	596.00	4.14	−1.02	3.52	−0.40
2.44	185.80	4.37	−1.15			9.91	607.00	4.54	−1.15	4.32	−0.63
2.51	188.92	4.53	−1.06	3.87	−0.65	10.01	617.00	3.44	−1.16		
2.55	190.71			3.78	−0.61	10.11	628.00	5.13	−1.28	4.31	−0.57
3.41	229.08	4.21	−1.04			10.21	638.17	4.97	−1.36	4.28	−0.58
3.51	233.54	4.36	−1.01	3.66	−0.41	10.31	648.33	5.00	−1.23	4.35	−0.40
3.61	238.00	3.56	−0.80			10.41	658.50	4.67	−1.58	4.15	−0.68
3.71	256.24	4.71	−1.22	3.92	−0.56	10.51	668.67	4.29	−1.35	3.99	−0.71
3.78	269.00			3.94	−0.67	10.61	678.83	4.45	−1.25	3.76	−0.48

APPENDIX B (continued)

Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*		Depth in core (m)	Age (1000 yr B.P.)	*Uvigerina* spp.		*C. wuellerstorfi*	
		$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$			$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$
4.21	277.32			3.98	−0.68	10.71	689.00	4.18	−1.11	3.55	−0.73
4.51	283.13			3.81	−0.68	10.81	694.50	4.66	−1.17	3.93	−0.59
10.91	700.00	4.71	−1.22			11.21	726.00	4.14	−1.37	3.60	−0.45
11.01	711.00	4.42	−1.44	3.72	−0.93	11.31	731.00	4.03	−1.08	3.47	−0.54
11.11	721.00	4.58	−1.37			11.41	740.00	4.65	−1.41	3.78	−0.76

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